Quenching and Heat Transfer Properties of Aged and Unaged Vegetable Oils

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Abstract

Vegetable oils may be potentially used as an alternative basestocks to petroleum oil for the formulation of quenchants. Comparative performance cooling curve of a number of vegetable oil basestocks commercially available in Brazil was reported previously. These basestocks included: soybean, canola, corn, cottonseed and sunflower oils. However, these particular vegetable oils exhibit very poor thermal-oxidative stability, relative to petroleum oil, which is attributable to their molecular composition. To address this specific deficiency which affects long-term performance, a number of additional vegetable oils with much more favorable molecular structure were examined including: peanuit (groundnut) oil and coconut oil. To assess the quenching performance compared to conventional and accelerated quenching oils, cooling curve performance according to ASTM D6200 for two bath temperatures (60 °C and 90 °C) was determined. In addition, effective heat transfer coefficients were calculated and compared. It is noteworthy that the vegetable oils evaluated did not exhibit classical film boiling or nucleate boiling behavior during quenching.

Keywords

Quench; Vegetable Oil; Heat Transfer; Oxidative Stability; Cooling Curve

Introduction

The most common used quenchants is water. However, petroleum oil (mineral oil) derived quenchants are used when lower cooling rates and more uniform cooling is desired for better distortion control and crack prevention of alloy steels. However, petroleum oil possesses a number of significant disadvantages including: 1) poor biodegradability (Jones, 1996), 2) toxicity (Henry, 1998), 3) flammability and 4) petroleum oil is not a renewable basestock (Erdman, 1998). Therefore, it is of continuing interest to identify a viable alternative to petroleum oil as a basestock for industrial oil formulation such as quenchants for heat treating applications (Erdman, 1998).

Currently vegetable oils are one of the most commonly identified alternative basestocks to petroleum oils primarily because they are biodegradable and are obtained from renewable sources. Brazil has shown interest in the behavior of soybean oil for use as coolants (and quenchants) and for lubrication formulation because it is a biodegradable renewable basestock and it represents 95% of all seed oil production in the country (Otero, 2011 and Souza, 2009). Soybean oil has shown excellent performance in various commercial applications (Souza, 2011). However, its oxidative instability and its narrow viscosity range substantially limits its use as a quenchant.

While palm oil (dende oil) occupies a prominent position on the world market, it is the second most produced seed oil behind only soybean oil, it is not currently produced at a high level in Brazil. Relative to soybean oil, palm oil contains a substantially higher saturated fatty ester content and significantly lower polyunsaturated acid content in the overall triglyceride structure of the two seed oils and is therefore more resistant to oxidation. This is because molecular double bonds, especially double bonds in conjugation which are in greater concentration in vegetable oils such as soybean oil, react more easily with oxygen to form free radicals leading to faster degradation when subjected to elevated temperatures as would be encountered during quenching of steel. Recently, it has been shown that, as expected, palm oil is significantly more oxidatively stable than soybean oil but still not as stable as petroleum oil (Belinato, 2011).

The objective of this work is to continue these studies by evaluating peanut oil and coconut oil. Peanut oil is often

used as the choise of vegetable oil for deep frying in the food preparation industry because of its higher smoke point and better thermal-oxidative stability (Tan, 2002). Coconut oil was selected because it contains an even greater amount of saturated fatty esters and lower degree of unsaturation in its triglyceride composition than any of the vegetable oils evaluated in these studies to date [5,8]. The results of oxidative stability testing and cooling curve comparison will be reported here.

Experimental Methods and Materials

The vegetable oils used for this work were purchased at the local market in São Carlos, São Paulo, Brazil, and were used in the as-purchased condition. The vegetable oils that were purchased included canola oil, cottonseed oil, corn oil, sunflower oil, and soybean oil commercially designated as "pure" soybean oil. Quenching performance of these oils was compared to two commercially available quenching oils: Micro Temp 157 a conventional "slow" oil and Micro Temp 153B an accelerated "fast" oil.

Viscosity was measured at 40 and 100°C according to ABNT NBR 10441-10/02. This method is comparable to, the Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids and Calculation of Dynamic Viscosity (ASTM D445-06). The time is measured for a fixed volume of liquid to flow under gravity through a glass capillary viscometer at a closely-controlled and known temperature. The kinematic viscosity determined value is the product of the measured flow time and the calibration constant of the viscometer. Two such determinations are needed from which to calculate a kinematic viscosity result that is the average of two acceptable determined values. The range of kinematic viscosities covered by this test method is from 0.2 to 300 000 mm^2s^{-1} at all temperatures.

Cooling curves were obtained under unagitated conditions according ASTM D6200-01, Standard Test Method for Determination of Cooling Characteristics of Quench Oils by Cooling Curve Analysis at bath temperatures of 40, 60, 80, 100, and 120 °C. This test method is based on the 12.5 mm dia. *x* 60 mm cylindrical INCONEL 600. After heating the probe in a furnace to 850 °C, it was then manually and rapidly immersed into 2,000 mL of the oil to be tested, which was contained in a tall-form stainless steel beaker. The probe temperature and cooling times are recorded at selected time intervals to establish a cooling temperature versus time curve.

The accelerated aging equipment used for this work was described previously by Farah (Farah, 2002 and Canale, 2005) which was based on the equipment reported earlier by Bashford and Mills (Bashford, 1984). For this test, a 2.7 L oil sample is placed in a metal beaker which was immersed in a constant temperature water bath where the temperature is cycled between 150 °C and 120 °C every 15 min. The accelerated oxidation was performed under agitation which was provided by using an air flow of 4 L per hour through the vegetable oil being tested. The oxidation test was conducted for 48 h for soybean oil and 60 h for oil palm (since palm oil was found to be significantly more stable) and interrupted every 12 h to determine the fluid viscosity at which time the fluid was returned to the aging system without adding more oil.

Results and Discussion

One of the reactions that occurs when a vegetable oil oxidizes is due to the double bond functionality to react with other double bonds resulting in an overall increase in molecular weight and viscosity (Belinato, 2011). Therefore, one method of monitoring oxidation of a vegetable oil is by monitoring the increase in fluid viscosity of the aging fluid. The test was conducted on uninhibited vegetable oils and the viscosity change from the fresh fluid, after 12, 24 36 and 48 hours is tabulated. The test was stopped after 48 hours because of the large viscosity increases obtained for all of the vegetable oils at this time. For reference, the viscosity change of two fully formulated petroleum oil quenchants was also evaluated. However, since essentially no viscosity change was observed, the testing time was extended to 60 hours at which time only minimal viscosity change was observed. These data were plotted and the results are shown in Fig. 1 and Table 1. The relative order of viscosity increase from best (peanut) to worst (corn) is: peanut < sunflower ≈ cottonseed ≈ soybean < coconut < canola < corn oil.

It is well known that petroleum oil based quenchants exhibit pronounced film-boiling and nucleate boiling (Komatsu, 2009). This is a disadvantage when faster high-temperature cooling is necessary, particularly for crack-sensitive, low-hardenability steels. In such cases,

additives are used to decrease the film boiling behavior by accelerating the wetting of the steel after immersion in oil for cooling. However, vegetable oils do not exhibit the same film boiling or nucleate boiling behavior during quenching as shown in Fig. 2. This is because of the very high boiling points exhibited by vegetable oils under atmospheric pressure conditions. Thus, the surface temperature of the steel decreases below the boiling point and cooling is predominantely by convection. The results obtained in this work are consistent with the relatively fast cooling process reported previously for vegetable oils (Souza, 2009 and Komatsu, 2009).

TABLE 1 VISCOSITY CHANGE WITH RESPECT TO TIME FOR A SERIES OF UNINHIBIED VEGETABLE OILS AND TWO FULLY FORMULATED COMMERCIAL PETROLEUM OIL QUENCHANTS

Aging time (hours)	0	12	24	36	48	60
Cottonseed	30.84	45.27	67.05	93.47	114.43	-
Sunflower	31.03	54.44	55.69	74.60	106.99	-
Corn	31.40	46.98	74.69	121.68	163.13	-
Soybean	29.80	41.07	52.76	94.99	119.67	-
Canola	33.45	59.53	-	87.28	144.84	-
Peanut	33.73	57.33	53.86	64.19	78.96	-
Coconut	26.32	29.80	49.20	92.40	124.10	-
Micro Temp 157	29.00	-	-	34.87	-	35.17
Micro Temp 153 B	40.00	-	-	48.51	-	50.58

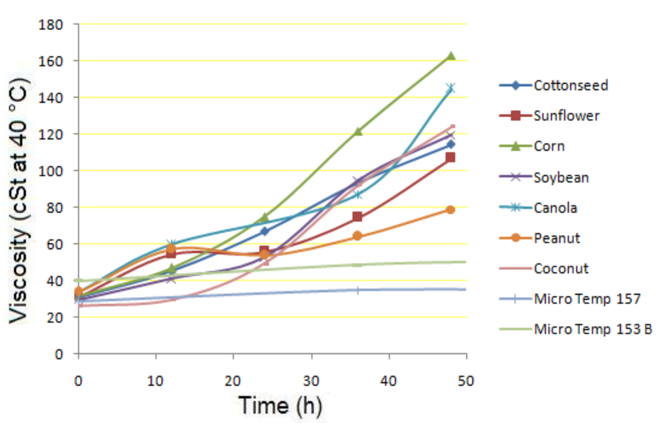

FIG. 1 COMPARISON OF THE VISCOSITY CHANGE WITH RESPECT TO TIME FOR A SERIES OF UNINHIBITED VEGETABL OILS. FOR REFERENCE, THE RESULTS OBTAINED FOR TWO FULLY FORMULATED PETROLEUM OIL QUENCHANTS ARE ALSO SHOWN

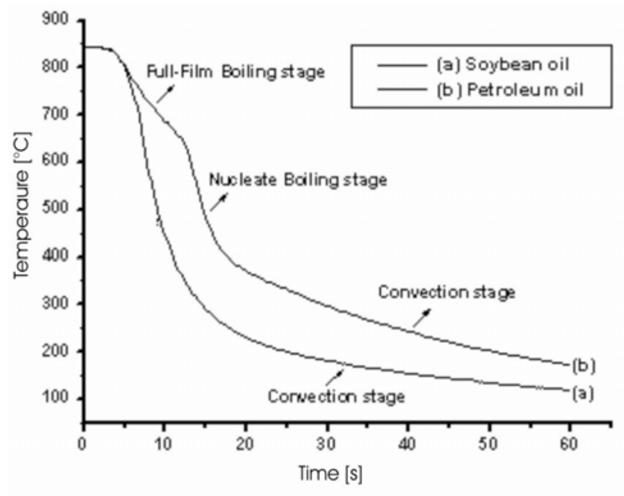

FIG. 2 COMPARATIVE ILLUSTRATION OF THE DIFFERENT COOLING MECHANISMS EXHIBITED BY PETROLEUM OIL AND A VEGETABLE OIL DURING QUENCHING

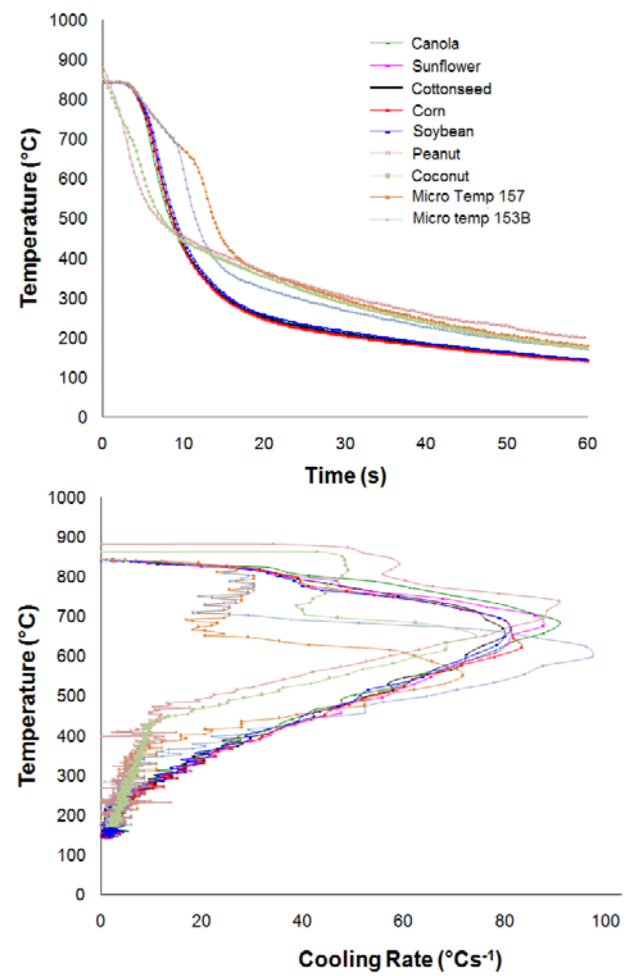

FIG. 3 COOLING TIME-TEMPERATURE AND COOLING RATE BEHAVIOR OF A SERIES OF VEGETABLE OILS AND TWO COMMERCIAL FULLY FORMULATED PETROLEUM OIL QUENCHANT REFERENCE FLUIDS

Most conventional cooling processes involving vaporizable quenchants possess four cooling mechanisms: 1) shock boiling, 2) film boiling, 3) nucleate boiling and 4) convection cooling processes. While shock fim boiling is not observable with the Inconel 600 probe with the thermocouple at the center, the other cooling mechanisms can be seen as shown in Figure 2. Since the ASTM D6200 standard 12.5 mm dia x 60 mm cylindrical Inconel 600 probe provides cooling rate and temperature vs. time at the core of probe, it is only possible to evaluate "average effective heat transfer coefficient (α_{ave})" [16]. During quenching, the value of α_{ave} is dependent on: surface temperature of the steel part (probe), mass and flow of the quenchant at the metal/quenchant (boundary) layer. Since the variation of the heat transfer coefficient during film boiling is typically sufficiently small is is possible to use average values (α_{ave}). During nucleate boiling and convective cooling, average effective heat transfer coefficients can be determined. In this paper, heat transfer coefficients were calculated according to the theory of regular conditions and the calculation procedure described previously by Kobasko, et. al. was used (Kobasko, 2010a and 2010b).

The cooling time-temperature curves and cooling rate curves, of the vegetable oils and of the two petroleum oil quenchant reference fluids, obtained in this work are shown in Fig. 3. With the exception of coconut oil, all of the vegetable oils behaved as depicted in Fig. 2 when compared to the petroleum oil quenchants. However, cooling curve behavior of the coconut oil, which possesses a significantly lower average molecular weight which would correspond to somewhat greater volatility than the other vegetable oils, does exhibit evidence of full-film boiling. The calculated average effective heat transfer coefficients both at 60 and 90 °C bath temperatures are summarized in Table 2.

TABLE 2 AVERAGE EFFECTIVE HEAT TRANSFER COEFFICIENT COMPARISON OF A SERIES OF VEGETABLE OILS WITH TWO COMMERCIAL FULLY FORMULATED PETROLEUM OIL QUENCHANTS

Heat Transfer Coefficient (W/m²K)								
Oil Condition	**New**				**Aged**			
Temperature (°C)	300 – 400		650 – 750		300 – 400		650 – 750	
Bath temperature (°C)	60	90	60	90	60	90	60	90
Cottonseed	319	320	1746	1982	745	1526	2083	1861
Sunflower	660	876	1627	1923	1323	1495	1997	2008
Corn	314	729	1613	1647	1455	1666	1054	943
Soybean	859	469	1630	1973	389	696	1982	2200
Canola	906	472	1560	1936	848	1048	1953	2251
Peanut	312	311	1691	1828	721	1099	1924	2168
Coconut	318	325	947	947	1356	1221	830	1257
Temperature (°C)	450		700		450		700	
Micro Temp 157	1790	-	587	-	-	-	-	-
Micro Temp 153 B	2060	-	705	-	-	-	-	-

The heat transfer coefficient data for fresh vegetable oils in Table 2 shows that all of the vegetable, with the exception of coconut oil, exhibit relatively high heat transfer coefficients in the higher temperature region (650-750 °C) region suggesting that the slow film-boiling process is not occurring. However, coconut oil does exhibit slower cooling in this region suggesting at least incipient film-boiling is occurring. Interestingly, the heat transfer coefficients in the lower temperature region (300-400 °C) are quite variable with no discernable trends. For example, at a 60 °C bath temperature; corn, coconut, cottonseed and peanut oils are substantially slower cooling than canola, sunflower or soybean oil. At the 90 °C bath temperature; coconut, cottonseed and peanut oils are slowest in this region, sunflower and corn oils are fastest with canola and soybean oils being similar to each other and intermediate between the other two groupings. At this time, the reason for this behaviour has not been determined. As expected, the petroleum oils exhibited slow cooling at higher temperature due to full-film boiling and faster cooling at lower temperature with the fast petroleum oil, MicroTemp 153B higher (larger) effective heat transfer coefficients than the slow (or conventional) petroleum oil quenchant, MicroTemp 157.

The effective heat transfer coefficients of the aged vegetable oils is more difficult to analyze. First of all, it is surprising that such a relative small change in heat transfer would result from a large change in fluid viscosity. This indicates that even though vegetable oil quenchant viscosity may increase, the overall heat transfer properties may not exhibit a correspondingly large change. The variability in the two temperature regions, (650-750 °C) and (300-400 °C) mostly follow the same trends observed 1) for the fresh, unaged oils with faster cooling in the high-temperature region and 2) slower cooling in the lower temperature region with coconut oil being the exception although the cooling rate differences between the two temperature regions is considerably closer in most cases than that observed for the unaged vegetable oils.

Conclusions

The oxidative stability of a series of vegetable oils was determined experimentally. Accordingly, the relative order of viscosity increase from best (peanut) to worst (corn) is: peanut < sunflower ≈ cottonseed ≈ soybean < coconut < canola < corn oil. These data show that at least in this test, the peanut oil was the most promising from the standpoint of oxidative stability. However, not surprisingly, the oxidative stability of none of these vegetable oils even closely rivaled the petroleum oil quenchants evaluated as reference fluids. Clearly, the addition of effective antioxidants is required. This work is in progress.

As with other quenching studies reported so far, with the exception of coconut oil, none of the other vegetable oils exhibited film boiling or nucleate boiling. Coconut oil, the vegetable oil evaluated with the lowest average molecular weight, and presumably greatest volatility, did appear to exhibit some full-film boiling behavior typical of what is observed for petroleum oils. These cooling behaviors were verified from the cooling curves and calculated average effective heat transfer coefficients.

Surprisingly, the significant increases in fluid viscosity obtained by ageing, were not reflected in substantial changes in heat transfer.

Research continues into the cooling mechanisms and effect of structure/performance on quenching behavior of vegetable oil both in their native state and after chemical modification. In addition, antioxidant studies are in progress and those results will be reported elsewhere.

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